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By F. H. Crawford and P. M. Tsai.

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The bands emitted by the ionized nitrogen molecule (assigned to a $^2\Sigma \rightarrow {}^2\Sigma$ transition) have been studied by a number of observers under a wide variety of conditions. The sources of most value, however, have been direct current discharges with a hollow cathode,[1] the electrodeless discharge[2] or high voltage discharges either in pure N_2 or with the addition of small amounts of helium.[3] In addition Childs[4] has used a direct current arc between tungsten electrodes—a source which develops very high rotational lines but gives only a very few vibrational transitions.

Experimental Methods.

The writers, experimenting with the slotted cathode designed by Frerichs, found that under certain conditions of operation great freedom from the usually very troublesome second positive bands of the neutral molecule resulted. The source consisted briefly of two heavy water-cooled electrodes, the cathode containing a transverse slot from which brilliant emission of the N_2^+ bands resulted at pressures of a few hundredths of a millimeter of mercury. It was found advantageous to replace the block-tin cathode by one of iron, since this permitted heavier currents (around .75 ampere with 400 volts drop across the tube), and, in addition, developed a few very faint and narrow iron lines. These were not sufficiently numerous to cause serious trouble when superposed on the band lines, and yet offered a delicate method of proving the absence of any accidental shifts of the band lines with respect to the iron standards placed on the plates before and after each nitrogen exposure.

A number of cathode-slit widths from around 2 to 5 mm. were employed, and in each case the pressure of the nitrogen was reduced to

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[1] Fassbender, Zeits. f. Physik **30,** 73 (1924); Frerichs, *ibid.* **35,** 683 (1926); Ornstein and van Wijk, *ibid.* **49,** 315 (1928); Coster and Brons, *ibid.* **73,** 747 (1932).

[2] Herzberg, Ann. der Physik **86,** 189 (1928).

[3] Merton and Pilley, Phil. Mag. **50,** 195 (1925); Parker, Phys. Rev. **44,** 90, 914 (1933).

[4] Childs, Proc. Roy. Soc. (A) **137,** 641 (1932).

such a value that the discharge was unstable, being almost ready to break over into a diffuse and feeble glow discharge with no visible emission from the slit in the cathode. Since the greatest freedom from the troublesome bands of N_2 resulted under these conditions, it was necessary to watch the discharge quite closely since a few minutes' discharge at a higher pressure would ruin the most desired bands by superposition of strong N_2 bands. It was found that, when the electrode from a small induction coil (such as that used for leak-testing purposes) was placed near enough the glass bulb containing the discharge to allow a continuous sparking to the glass, much more steady operation resulted. This was particularly useful in the longest exposures, which were made in the first (and where possible the second) order of a 21-foot grating giving a dispersion of 1 Å/mm. in the second order. The exposures ran from 2 to 28 hours in length. Eastman "33" plates were used for the first order, "50's" for the second, and the "3G" plates for all green regions. The usual iron comparisons were made with an arc of the Bureau of Standards specifications,[5] the standard lines used being those recommended by the International Astronomical Union.[6] The plates were measured to .001 *mm* and in the second order plates and the R branches where overlapping is least the results are dependable to less than $\pm$ .005 Å. Near the origins, however, and at the heads the uncertainty is hard to estimate, but is certainly greater.

Results.

This source developed the $\Delta v = 0, +1$ and $+2$ sequences quite intensely, and gave the first three members of the $\Delta v = +3$ sequence with usable intensity and very high purity. The freedom from appreciable overlapping of N_2 bands has enabled the rotational fine structure of the following bands to be determined (2–2) λ3858, (3–4) λ4166.8–4166.4, (5–7) λ4486, (6–8) λ4466.6, (0–3) λ5228, (1–4) λ5148.8, and (2–5) λ5076.5. The (3–4) band was particularly important, since Coster and Brons were not able to follow the (3–5) band below $K = 4$ and settle the question as to the precise extent of the perturbation of the $v' = 3$ level and the proper assignment of spin doublet components. New data on this band is also included. A few lines of the (3–6) band were observed but were not strong enough to be of much value in the analysis.

[5] Meggers, Kiess and Burns, Bull. Bureau of Stds, **19,** 263 (1923–4).

[6] Trans. Int. Astron. Union III, 84 (1928).

The rotational assignments of the new bands and the vacuum frequencies are given in Table I. The frequencies of the origins were determined graphically from the first half dozen or so lines of each branch and are compared with those computed from the origin formula of Coster and Brons in Table IV. Except in bands involving the perturbed upper levels $v' = 1$, $v' = 3$, and $v' = 5$, the spin doubling was resolved only for the higher rotational lines where theoretically the spin members should be almost equally intense. In the perturbed bands involving $v' = 1$ and $v' = 5$ only one level is perturbed, and the fact that the perturbed members of each doublet to the *low* frequency *before* the perturbation and to the *high* frequency *above* this point are definitely more intense shows these to have originated on the $T_1(K + \frac{1}{2})$ levels. Accordingly, to save space, the $R_1(K)$, $R_2(K)$ and $P_1(K)$ and $P_2(K)$ lines are listed under their common K value. The R_1 *and* P_1 lines are in every case listed *above* the R_2 *and* P_2 lines, where of course the former are of lower frequency *before*, and of higher frequency than the latter *after* the perturbation. For convenience the most perturbed lines immediately before and immediately after the perturbation are designated by an asterisk. Where three lines are entered for a single K value, the central one is the T_2 line and the outer ones the T_1 lines. The corresponding double differences $\Delta_2 T'$ and $\Delta_2 T''$ are given, respectively, in Tables II and III with the same convention employed, where for purposes of comparison the corresponding values from other bands, as remeasured by us, are included. Where we have observed only one band involving a given level, comparison values are given from Parker and from Coster and Brons.

In the analysis of the (1–4) λ5148.8 band, which was so nearly free from impurities that almost every measurable line on the plate was assigned a place in the band, it was found impossible to obtain agreement with the $\Delta_2 T_1'(K)$ values given by Coster and Brons for the lines $K = 13$ and $K = 14$. Accordingly the three bands (1–1) (1–2) and (1–3) were completely remeasured, with the result that a natural assignment of lines was discovered which agreed well with the λ5148.8 band and at the same time gave a more nearly regular set of $\Delta_2 T_1'(K)$ values for $v' = 1$. Since the corresponding $\Delta_2 T''(K)$ values agreed quite satisfactorily with the 4 independent sets of values from other bands, the agreement can hardly be accidental. In Table I-A these branch assignments and frequencies for the K values near the point in question are recorded. In addition the values of $\Delta_2 T_1'(K) \,/\, (4K + 2)$

are computed for each K value and may be compared with the average value computed from the data of Coster and Brons (Column I) from the (1–2) and (1–3) bands. The sudden and irregular increase at $K = 13$ and 14 is seen to be replaced by fluctuations which must be regarded as entirely random.

The great reduction of overlapping N_2 bands on the best plates has also permitted us to analyze the (3–4) band and to extend the analysis

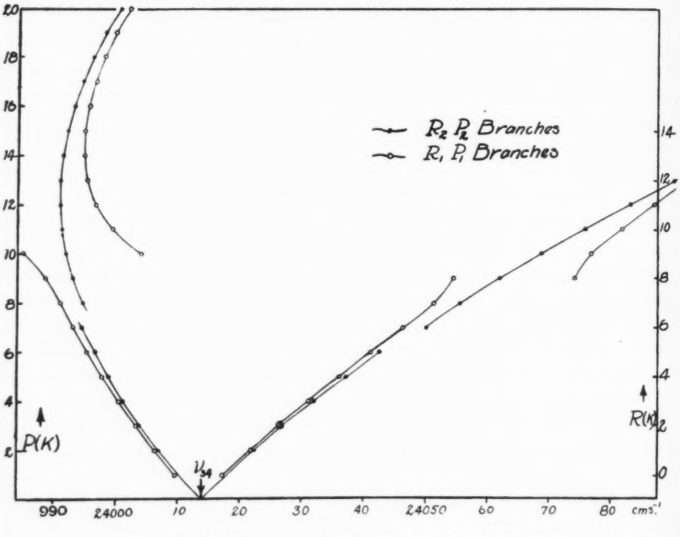

FIGURE 1. Fortrat Diagram of the (3–4) λ4166.8–.4 band showing the double perturbation, the more violent of which is responsible for the formation of the double P branch which results in the double headed appearance so characteristic of low dispersion photographs.

of the (3–5) band to the origin. The results indicate, as found earlier by Coster and Brons, that both spin levels are perturbed, the $T_1(K + \frac{1}{2})$ levels (the reasons for the assignment are considered below) suffering a very large perturbation (maximum shift about 11 cms.$^{-1}$) centering around $K' = 9$, while the $T_2(K - \frac{1}{2})$ levels suffer a much smaller perturbation (maximum shift about 1 cm.$^{-1}$) centering between $K' = 6$ and $K' = 7$. Although Coster and Brons

suggested the possibility of a further perturbation nearer the origin, we have found no definite evidence for it. The early lines do seem to be abnormally low in intensity but fall quite smoothly on the normal Fortrat curves. (See Fig. 1.)

The rotational constants B_v' and B_v'' have been computed from the double differences given in Tables II and III. Where only one level is perturbed the other has been used for this purpose. Where both are perturbed a curve with smoothly turning tangent was drawn through the regions of perturbation and B-values computed from this. If we write

$$\Delta T(K) = (4K + 2)\,[B_v + 2D_v(K^2 + K + 1) + \cdots]$$

the values of $\Delta T(K) \,/\, (4K + 2)$ should give sensibly B_v as long as D_v is so small as to make no appreciable contributions. But as D_v' is of the order of 4.3×10^{-6} and D_v'' is smaller we see that, even for $K = 8$, the contributions of this term can hardly be expected to affect the value of $\Delta T(K) \,/\, (4K + 2)$ in the third decimal. Hence fluctuations of this quantity for $K \leq 8$ must be regarded as due to experimental uncertainties or the residual effects of perturbations. Hence average values for the first 8 members of each set were taken as the true B_v values. The values so determined are compared in Table V with the calculated values obtained from the empirical expressions given by Coster and Brons and by Parker.

Perturbations.

The previous designation[7] of the perturbed levels in the $v' = 1$ and $v' = 5$ state as T_1 levels (*i. e.* belonging to levels with $J = K + \frac{1}{2}$) is completely in agreement with our results. The situation is, however, much more complicated in bands involving the $v' = 3$ level, and it is unfortunate that only the (3–4) and (3–5) bands could be observed.

Since in a normal spin doublet the member involving the T_1 level is stronger than that involving the T_2 level in the ratio of $K + 1/K$, provided the perturbation does not too much modify the normal intensity distribution, the determination of which component is more intense on either side of and sufficiently far from the perturbation should settle the question of assignment. For this purpose densitometer records were made from both first and second order plates on a recording thermocouple densitometer constructed by one of us (F.H.C.). In use a linear magnification of about 50 : 1 was employed

[7] *Loc. cit.* Refs. 1 and 3.

and, in order to avoid as much as possible irregularities due to plate grain, dust, scratches on the emulsion, etc., the thermocouple was adjusted so as to integrate the light from a narrow illuminated strip on the plate, which never covered less than 5 or 6 mm. of the length

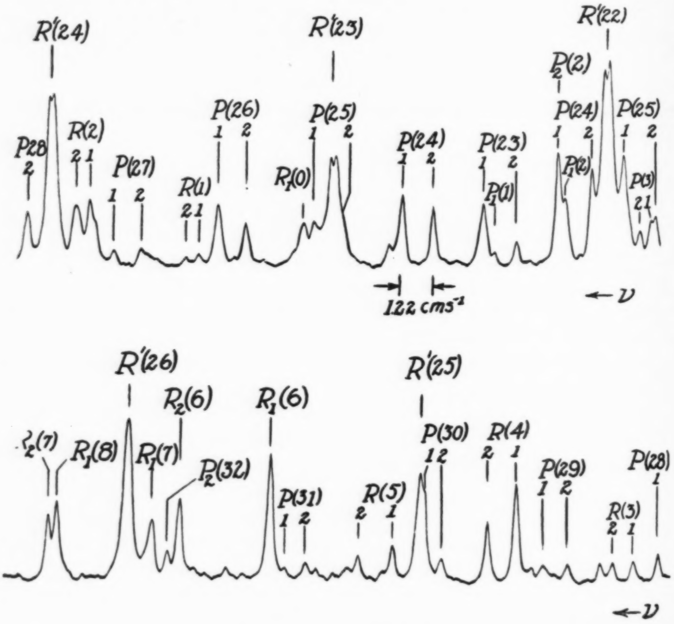

FIGURE 2. Microphotometer record of a portion of the (3–4) λ4166.8–.4 band where the lines not marked are of spurious origin. The perturbation in the R_2 lines reaches its maximum between $R_2(5)$ and $R_2(6)$ while that of the R_1 lines is near $R_2(8)$ at the edge of the figure. The two portions are continuous records beginning in the upper right hand corner and continuing to the lower left hand corner. The primed R lines belong to the overlapping (2–3) band. The freedom from extraneous N_2 lines is striking.

of a line. The resolving power was sufficient to indicate any line structure which could be seen on a direct 15-fold enlargement made from the original plate with contrast paper and gave definite reproducible recordings of lines so faint that they had earlier been

measured on a visual comparator but marked doubtful. In the case of the (3–4) band the early R-lines, $R(1)$, $R(2)$, $R(3)$, $R(4)$, $R(5)$ and $R(6)$ all showed the $-$ component[8] definitely stronger, though the difference was very slight except for $R(4)$ and $R(5)$, and the $R(2)$ doublet certainly involves some superposition. *Above* the perturbation the $+$ components are fainter than the $-$ but gradually increase in intensity, becoming almost identical at $R(14)$ and definitely stronger for $R(17)$. Above this point the (4–5) band intervenes and prevents further observation. Unfortunately, the early P lines are in much too crowded a region to allow accurate densitometry. Of the favorably located higher ones, $P(23)$, $P(24)$, and $P(26)$ have the $+$ component stronger and only $P(28)$ shows the reverse. $P(28)$ is quite close to $R(24)$ of the (2–3) band. (See Fig. 2.) The intensity asymmetry of these high P lines is rather greater than one would expect for such high K values.

The results in the case of the (3–5) band are slightly less decisive. Here, as in the (3–4) band, the $-$ component is more intense for $R(1)$ and $R(4)$ while $R(6)+$ and $R(6)-$ are of almost identical intensity. In the case of $R(5)$, on the other hand, the $-$ component is definitely weaker. This may possibly be due to superposition, since $R(5)+$ is nearly as intense as $R(4)-$ and $R(6)-$, a fact not in harmony with the usual regular alternating intensity. The other early R lines are all unfavorably situated. Above the perturbation $R(16)$, $R(18)$, $R(20)$, $R(25)$, and $R(27)$ [the (4–6) band obscures the others above $R(20)$] show the $+$ component stronger, while $R(15)$, $R(17)$ and $R(19)$ show the reverse. Of the P lines which are in the open we find $P(20)$, $P(22)$, $P(24)$, $P(26)$, and $P(29)$ with the $+$ component stronger, while $P(21)$ and $P(25)$ show the reverse. These results, then, seem to point fairly conclusively to the inference that the largely perturbed lines of the $v' = 3$ level originate on $T_1(K + \frac{1}{2})$ levels rather than on $T_2(K - \frac{1}{2})$ levels, as Coster and Brons concluded. It should be emphasized that they based their inference entirely on the (3–5) band—where the evidence is less unambiguous than for the (3–4) band. The rather small asymmetry of the $R(1)$, $R(2)$, and $R(3)$ lines is possibly accounted for by the following considerations. Suppose we regard the early $T_1(K + \frac{1}{2})$ levels as being perturbed *below* their corresponding $T_2(K - \frac{1}{2})$ levels in the $v' = 3$ state, while for the $v'' = 4$ and $v'' = 5$ states they are of course almost

[8] For brevity the high frequency member of a pair or group will be called the $+$ and the low frequency the $-$ component.

indistinguishably close to them (see Fig. 3). Then the fragmentary Q branch, which should be more intense at the origin and rapidly vanish in intensity with K, involves transitions such that, for example, with $\Delta J = 0$ and $\Delta K = -1$ the corresponding ${}^RQ_{21}(K)$ line will practically coincide with $R_2(K)$. But $R_2(K)$ is by our hypothesis the $+$ component for low K values and should therefore have a slightly enhanced intensity, thus tending to make the $R(K)$ doublets more nearly symmetrical in intensity than otherwise. If we suppose

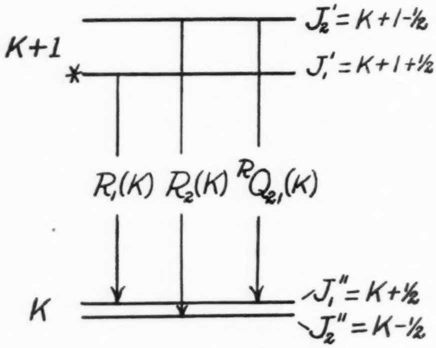

FIGURE 3. Transitions giving R and ${}^RQ$ branch lines before the main perturbation, in which case the perturbed level (*) in the upper ${}^2\Sigma$ state lies *below* the $T_2(K - \frac{1}{2})$ level. If the perturbed level were called a T_2 level, the $-$ component of an R doublet would be enhanced.

the lower spin level of the upper ${}^2\Sigma$ state is T_2 level then the ${}^RQ_{21}(K)$ line will fall on the $R_1(K)$ line and produce greater asymmetry than otherwise. This certainly seems contrary to our observations.

As a result, in disagreement with Coster and Brons, we have identified the $v' = 3$ rotational spin sub-levels with the major perturbation as T_1 levels and have so arranged the data in the tables. It must be pointed out, however, that the accidental superposition of faint and unsuspected lines, together with a disturbance of normal intensity considerations, may invalidate the above reasoning. Statistically the former possibility seems extremely unlikely—while at points sufficiently remote from the perturbation (and, due to its asymmetry, it should affect the intensity of the perturbed lines for a

longer distance above than below the displacement maximum, see Fig. 4) we should certainly find the usual criteria applying.

To represent the course of the perturbation of the $v' = 3$ levels when both the T_1 and T_2 levels are disturbed, it is necessary to pass as smooth a curve as possible through the less perturbed lines and then

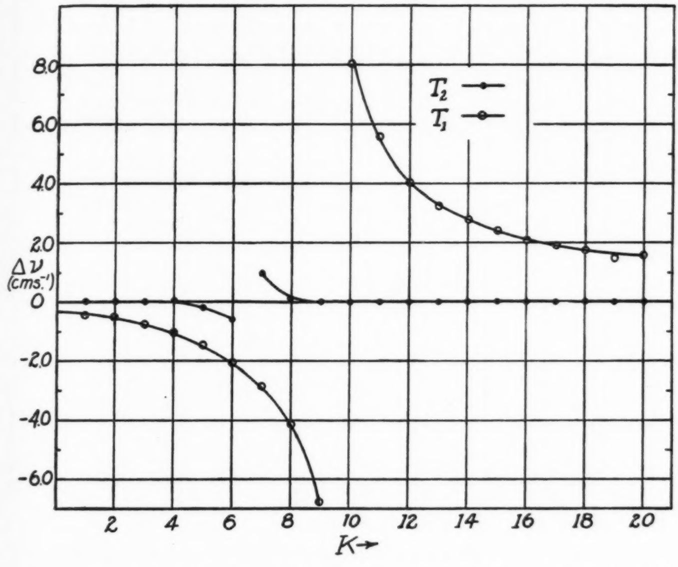

FIGURE 4. Actual displacements of the $T_1'(K + \frac{1}{2})$ and $T_2'(K - \frac{1}{2})$ levels from their smoothed values plotted against initial quantum number for the (3–5) λ4554.4–.2 band. See Table VI.

determine the frequency shift of the observed lines from this. In Table VI under "smoothed values," columns II and VII, are given these values for the R and P branches of the (3–5) band. They actually form a continuous set, as the regular progression of the first differences shows. The values of $R_1(K) - R_{smoothed}$, $P_1(K) - P_{smoothed}$, $R_2(K) - R_{smoothed}$, and $P_2(K) - P_{smoothed}$, are then given in columns X, XI, XII and XIII, respectively. Since the rows in Table VI are arranged according to common *initial* K values, the rows of X and

XI and of XII and XIII may be averaged directly. The results are shown graphically as a function of K' in Fig. 4.

In order to compare with these the results from the (3–4) band, it is possible to repeat the above process, though we have chosen to smooth the double differences, $\Delta_2 T'(K)$, and represent the departures

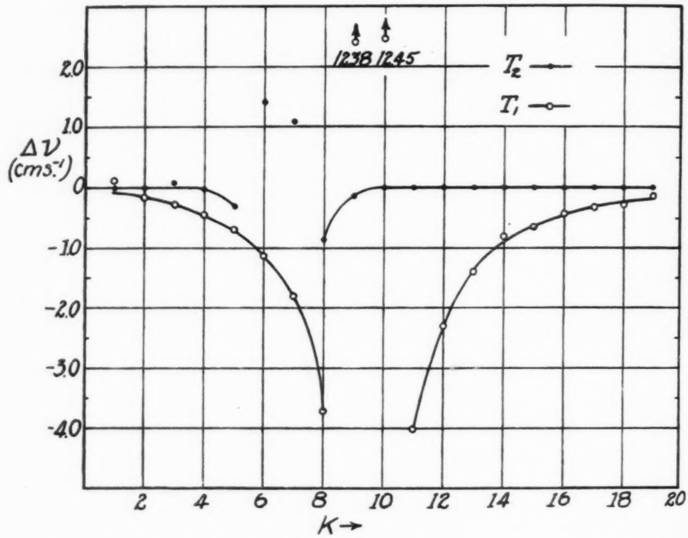

FIGURE 5. Graph showing the departures from smoothed $\Delta_2 T'$ values of the observed $\Delta_2 T_1'$ and $\Delta_2 T_2'$ values for $v' = 3$ as averaged from the (3–4) and (3–5) bands. Here negative values indicate closer spacing of the rotational levels, and positive values wider spacing than the normal.

of the observed values, $\Delta_2 T_1'(K)$ and $\Delta_2 T_2'(K)$, from these for the two bands. The results are given in Table VII and graphed in Fig. 5. The gradual increase of crowding of the rotational levels as the perturbation is approached, is shown by the rapid falling of the curves, while their gradual spreading out to the normal separation above the perturbation is indicated by the subsequent rise after the break. The two isolated positive points in each case arise from the fact that the separations of levels just above from those just below the perturbation are being measured. Since they represent the

absolute value of the *deficit* of height of a rotational level *below* and of the *excess* height of another (2 units of K' higher) *above* the perturbation, they must be above the axis. Since the perturbing state is presumably a $^2\Pi$ state, we infer that one member perturbs the T_1 levels violently near $K' = 9$ and $K' = 10$ while the other affects the T_1 levels less strongly, the center of perturbation being between $K' = 6$ and $K' = 7$.

In conclusion, we wish to express our indebtedness to the Rumford Fund of the American Academy for a generous grant used in the construction of the densitometer employed in this work. It is also a pleasure to express our obligation to Mrs. Kyung J. S. Tsai for her valuable assistance in the computation and checking of numerical results.

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TABLE I.

ROTATIONAL FREQUENCIES.

(2–2) λ3857.9 Band. $\nu_{22} = 25939.85\ cm^{-1}$

K	R Branch	P Branch	K	R Branch	P Branch
0	25943.74	—			
1	47.98	25935.76	16	26047.55	25914.01
2	52.71	32.48	17	56.25	14.86
3	57.50	29.30	18	65.41	15.95
4	62.88	26.16	19	74.89	17.00
5	68.25	23.78	20	84.58	18.66
6	74.08	21.36	21	94.43	20.77
7	80.14	19.34	22	104.83	—
8	86.57	17.49	23	15.39	—
9	93.17	15.95	24	25.96	—
10	26000.00	14.86	25	37.19	—
11	07.31	14.01	26	48.46	—
12	14.68	13.55	27	60.25	—
13	22.48	13.13	28	71.69	—
14	30.51	13.13	29	83.87	—
15	38.97	13.55	30	96.04	—
			31	208.52	—
			32	20.97	—

(3–4) λ4166.8–.4 $\nu_{34} = 24013.90\ cm^{-1}$

K	R Branch	P Branch	K	R Branch	P Branch
0	24017.48	—	7	24051.20*	23993.18
1	21.84	24009.55		55.50	94.43
	22.80	—	8	55.20*	91.05*
2	26.38	06.45		61.91	94.73
	26.98	06.95		74.17*	—
3	31.14	03.33	9	76.77*	88.50*
	31.98	03.80		68.70	92.88
4	36.06	00.48	10	81.84	85.00*
	37.23	01.15		75.81	91.89
5	41.20	23997.88		—	04.09*
	42.57	98.80			
			11	87.29	99.40*
6	46.30	95.49		83.18	91.48
	50.04	96.61			

* Perturbed lines near maximum of perturbation.

TABLE I.—ROTATIONAL FREQUENCIES—(*Continued*).

(3–4) λ4166.8–.4 $\nu_{34} = 24013.90\ \mathrm{cm}^{-1}$—(*Continued*).

K	R Branch	P Branch	K	R Branch	P Branch
12	24094.19	23996.61	19	24155.10	23999.70
	90.88	91.05		—	97.88
13	24101.72	95.23	20	65.15	24001.87
	098.91	91.05		63.70	00.48
14	109.73	94.73			
	107.32	91.48	21	75.47	04.09
15	17.87	94.73		74.20	02.63
	15.97	92.14	22	86.22	06.95
				84.89	05.51
16	24126.83	23995.49	23	—	10.05
	24.91	93.18		—	08.65
17	35.92	96.61	24	208.49	13.36
	34.16	94.43		207.30	12.14
18	45.28	97.88			
	43.79	96.05			

(3–5) λ4554.4–.2 $\nu_{35} = 21970.9\ \mathrm{cm}^{-1}$

0	21974.49	0	—	9	22035.36*	9	21946.99*
1	78.74	1	21966.60†		27.26		51.41
	79.26		—	10	40.36*	10	43.98*
2	83.14	2	63.34		34.72		50.82
	83.82		63.77		—		63.13*
3	88.17	3	60.44	11	46.71	11	58.83*
	89.11		60.90		42.90		50.82
4	93.30	4	57.66	12	54.11	12	56.42*
	94.50		58.39		50.87		50.82
5	98.62	5	55.26	13	62.19	13	55.63
	22000.06		56.42		59.42		51.41
6	03.97	6	53.02	14	70.79	14	55.63
	07.74		54.27		68.31		52.40
7	09.18*	7	50.82	15	79.55	15	56.42
	13.51		52.40		77.50		53.61
8	13.51*	8	49.18*				
	20.09		53.02	16	88.96	16	57.66
	32.41*		—		87.06		55.26

* Perturbed lines near maximum of perturbation.

† Superposed by another line.

TABLE I.—ROTATIONAL FREQUENCIES—(*Continued*).

(3–5) λ4554.4–.2 ν_{35} = 21970.9 cm^{-1}—(*Continued*).

K	*R* Branch		*P* Branch	*K*	*R* Branch	*P* Branch
17	22098.73	17	21959.35	23	22164.90	21977.65
	96.94		57.27		63.71	76.28
18	22108.85	18	61.47	24	77.16	82.04
	07.25		59.57		76.06	80.77
19	19.42	19	63.96	25	89.69	86.67
	17.84		62.28		88.60	85.38
20	30.34	20	66.60†			
	28.83		65.23	26	22202.63	
21	41.67	21	70.10		01.50	
	40.27		68.51	27	15.80	
22	53.01	22	73.75		14.93	
	51.82		72.25	28	29.41	
					28.42	

(5–7) λ4486 ν_{57} = 22307.5 cm^{-1}

K	*R* Branch	*P* Branch	*K*	*R* Branch	*P* Branch
0	—	—	10	22368.51	22287.54
1	—	—		366.26	284.92
	—	—			
2	22318.68	22299.58	11	375.60	286.78
	19.96	300.38		373.48	284.31
3	321.40*	297.28	12	383.01	286.50
	324.36	297.61		381.10	284.31
	330.62*	—	13	390.75	286.50
4	322.81*	93.98*		389.01	284.31
	329.36	95.13	14	398.83	286.78
	332.99*	—		397.22	284.92
5	—	289.48*	15	407.13	287.16
	334.41	292.36		405.60	285.59
	337.90*	298.63*			
			16	415.78	288.29
6	343.38*	293.98*		414.35	286.50
	340.36	290.07	17	424.77	289.48
7	349.27	291.61		423.30	287.54
	346.32	288.29	18	434.07	291.13
8	355.28	290.07		432.75	289.48
	352.68	286.78	19	443.94	292.94
9	361.77	288.48		442.26	291.61
	359.25	285.59	20	453.51	295.13
				452.35	293.98

* Perturbed lines near maximum of perturbation.

† Superposed by another line.

TABLE I.—Rotational Frequencies—(*Continued*).

(5–7) λ4486 ν_{57} = 22307.5 cm^{-1}—(*Continued.*)

K	*R* Branch	*P* Branch	*K*	*R* Branch	*P* Branch
21	—	—	23	—	22303.65
22	22474.19	22300.92		—	302.52
	472.80	299.58	24	22495.98	307.08
				494.99	305.87

(6–8) λ4466.6 ν_{68} = 22406.55 cm^{-1}

K	*R* Branch	*P* Branch	*K*	*R* Branch	*P* Branch
0	22410.23	—	14	22492.15	22382.10
1	14.35	22402.98	15	99.76	82.10
2	18.67	399.62			
3	23.30	96.67	16	507.77	82.36
4	28.22	94.03		.95	—
5	33.36	91.45	17	16.37	83.49
			18	24.87	84.81
6	38.84	89.01		25.23	—
7	44.60	87.43	19	33.66	85.91
8	50.54	85.91		34.12	—
9	56.77	84.63	20	42.80	87.43
10	63.29	83.49		43.15	87.64
11	70.11	82.77	21	52.28†	89.78
12	77.29	82.36		53.28†	—
13	84.45	82.10			

(0–3) λ5228.3 ν_{03} = 19139.7 cm^{-1}

K	*R* Branch	*P* Branch	*K*	*R* Branch	*P* Branch
0	19143.73	—	11	19217.09	19121.63
1	48.30	19136.08	12	26.30	22.49
2	53.32	32.52	13	35.92	23.83
3	58.74	29.71	14	45.89	25.42
4	64.55	27.16	15	56.28	27.78
5	70.81	25.42			
			16	67.27	30.37
6	77.47	23.58	17	78.30	33.25
7	84.56	22.49	18	89.81	36.65
8	92.06	21.65		90.04	
9	19200.00	21.26	19	19301.87	40.47
10	08.36	21.26		02.02	
			20	14.39	44.76
				14.53	

† Edges of broad band.

TABLE I.—Rotational Frequencies—(*Continued*).

(0–3) λ5228.3 ν_{03} = 19139.7 cm^{-1}—(*Continued*).

K	*R* Branch	*P* Branch	*K*	*R* Branch	*P* Branch
21	19327.15	19149.46	25		19172.21
	27.53				72.50
22	40.52	54.49			
	40.98	54.74	26		79.05
23	54.20	59.97			79.37
	54.68	60.21	27		86.19
24	68.42	65.85			86.51
	68.81	66.16	28		93.82
					94.24

(1–4) λ5148.8 ν_{14} = 19434.75 cm^{-1}

K	*R* Branch	*P* Branch	*K*	*R* Branch	*P* Branch
0	19439.00	—	15	19551.41	19426.64*
1	—	19430.95		49.81	22.81
2	48.53	(27.95)			
3	53.72	25.33	16	61.93	27.71*
4	59.53	22.59		60.52	25.33
5	65.81	20.73	17	72.96	29.88
				71.54	28.20
6	72.20	18.98	18		32.94
7	79.11	17.76			31.61
8	86.51	16.90	19		36.46
9	93.98	16.44			35.34
	94.38		20		40.58
10	01.97	16.44			39.50
	19502.64				
			21		45.02
11	09.58*	16.90			44.08
	11.21		22		50.00
12	16.23*	16.90			49.07
	20.29	17.76	23		55.25
13	33.45*	17.33*			54.45
	29.70	18.98	24		62.00
14	41.80*	16.44*			61.10
	39.56	20.73			

Values in parentheses are interpolated graphically.

TABLE I.—ROTATIONAL FREQUENCIES—(*Continued*).

(2–5) $\lambda 5076.5$ $\nu_{25} = 19710.4$ cms^{-1}

K	R Branch	P Branch	K	R Branch	P Branch
0	(19714.53)	—	11	19785.64	19692.70
1	19718.93	19706.67	12	94.58	93.46
2	23.94	03.63	13	(803.91)	94.69
3	29.23*	00.61	14	19813.43	96.24
4	34.95	19698.19	15	(823.44)	98.19
5	41.01	96.24			
			16	34.00	19700.61
6	47.39	94.69	17	(844.87)	03.63
7	54.17	93.46	18	56.01	706.67
8	61.53	92.70	19	(867.68)	710.12
9	69.18	92.26	20	79.68	13.71
10	76.56	92.26			
			21	92.12	18.26
			22	905.08	23.22

Values in parentheses are interpolated graphically.

TABLE I-A.

C and B $\frac{\Delta_2 T'}{(4K+2)}$	K	(1–1) λ3884 R	(1–1) λ3884 P	$\frac{\Delta_2 T'}{(4K+2)}$	(1–2) λ4236.5 R	(1–2) λ4236.5 P	$\frac{\Delta_2 T'}{(4K+2)}$	(1–3) λ4651.9 R	(1–3) λ4651.9 P	$\frac{\Delta_2 T'}{(4K+2)}$
	11	25830.30*	25736.99*		23690.53*	23597.75*		21583.55	21490.33*	
2.0486		31.71	37.37	2.0509	692.04	97.91	2.0463	85.11	91.17	2.0421
	12	35.41*	36.06*		696.05	97.17*		89.69	90.33*	
2.0500		39.41	36.99	2.0484	23700.14	97.75	2.0478	93.75	91.17	2.0516
	13	—	35.01*		712.52	96.39*		06.41	90.33*	
2.0794		47.34	36.50	2.0525	708.57	97.91	2.0492	02.54	91.85	2.0498
	14	57.83*	32.57*		19.75	94.45*		14.09	88.97*	
2.1196		55.62	36.77	2.0491	17.38	98.56	2.0486	11.90	92.95	2.0508
	15	65.79*	40.88*		28.15	23603.31*		23.23	98.56*	
2.0490		64.11	36.99	2.0503	26.50	599.50	2.0483	21.54	94.67	2.0462
	16	74.32	39.90		37.27	602.96		32.96	98.56*	
2.0484		72.75	37.37	2.0512	35.93	00.79	2.0476	31.62	96.44	2.0481

TABLE II.

$\Delta_2 T'(K)$ Values

$v' = 0$			$v' = 1$					
				(1–1)	(1–2)	(1–3)	(1–4)
K	Average†	λ5228.3	K	3884.3	4236.5	4651.9	5148.8
1	12.39	12.22	1	12.62	12.49	12.66	12.26
2	20.77	20.80	2	20.53	20.55	20.72	20.58
3	29.02	29.03	3	28.80	28.63	28.74	28.39
4	37.37	37.39	4	37.13	37.30	37.10	36.94
5	45.56	45.39	5	45.13	45.28	45.00	45.08
6	54.02	53.89	6	53.20	53.27	53.15	53.22
7	62.18	62.07	7	61.34	61.50	61.56	61.35
8	70.48	70.41	8	69.55	69.74	69.70	69.61
9	78.81	78.74	9	77.82	77.76	77.67	77.74
10	87.15	87.10	10	85.70	85.63	85.36	85.53
11	95.46	95.44	11	93.31	92.78	93.22	
12	103.56	103.81		94.34	94.13	93.94	(93.50)$^{+}$
13	112.04	112.09	12	99.35	98.88	99.35	99.33
14	120.36	120.47		102.42	102.39	102.58	102.53
15	128.50	128.50	13	—	116.13	116.08	116.12
				110.84	110.66	110.69	110.72
16	136.733	136.90	14	125.26	125.30	125.12	125.36
	.600	—		118.85	118.82	118.95	118.83
17	144.960	145.05	15	124.91	124.84	124.67	124.77
	.910	—		127.12	127.00	126.87	127.00
18	153.170	153.28					
	.150	—	16	134.42	134.31	134.40	134.22
19	161.443	161.48		135.38	135.14	135.18	135.19
	.350	—	17	142.90	142.82	142.89	143.08
20	169.69	169.70		143.73	143.26	143.52	143.34
	.69	—	18	150.95	151.13	151.27	—
				151.43	151.47	151.53	—
21	177.88	177.88					
	.88						
22	186.06	186.03					
	.15	.24					
23	194.30	194.23					
	.36	.47					
24	202.57	202.57					
	.54	.65					

†Av. from λλ3914, 4278, 4709 and 5228.

( ) calculated values.

$^{+}$Average of $\Delta_2 T_1'$ and $\Delta_2 T_2'$ values.

TABLE II.—(*Continued*).

$\Delta_2 T'(K)$ Values

$v' = 2$

K	(2–2) 3857.9	(2–3) 4199.2	(2–4) 4599.9	(2–5) 5076.5
1	12.22	12.05	12.20	12.26
2	20.23	20.18	19.94	20.31
3	28.20	28.20	28.42	28.62
4	36.72	36.35	36.51	36.76
5	44.47	44.57	44.59	44.77
6	52.72	52.59	52.67	52.70
7	60.80	60.67	60.95	60.71
8	69.08	68.80	68.85	68.82
9	77.22	76.91	77.27	76.92
10	85.14	84.99	84.97	84.30
11	93.30	93.20	93.06	92.94
12	101.13	101.11	101.35	101.12
13	109.35	109.37	108.98	109.22
14	117.38	117.35	117.11	117.19
15	125.42	125.46	125.30	125.25
16	133.54	133.53	133.81	133.39
17	141.39	141.52	141.45	141.24
18	149.46	149.62	148.87	149.34
19	157.89	157.71	157.53	(157.56)
20	165.92	165.50	165.64	165.97
21	173.66	173.71	173.80	(173.86)
22		181.75	181.92	181.86
23		189.73	189.67	
24			197.68	
25			205.89	
26			213.81	
27			221.38	
28			228.79	
29			237.17	
30			245.78	
31			254.02	
32			261.59	

TABLE II.—(*Continued*).

$\Delta_2 T'(K)$ VALUES

$v' = 3$

K	(3–4) 4166.8 4166.4	(3–5) 4554.4 4553.2	K	(3–4) 4166.8 4166.4	(3–5) 4554.4 4553.2
1	12.29	12.14	14	115.00	115.16
	—	—		115.84	115.91
2	19.93	19.80	15	123.14	123.13
	20.03	20.05		123.83	123.89
3	27.81	27.73			
	28.18	28.21	16	131.34	131.30
4	35.58	35.64		131.73	131.80
	36.08	36.11	17	139.31	139.38
5	43.32	43.36		139.73	139.67
	43.77	43.64	18	147.40	147.38
				147.74	147.68
6	50.81	50.95	19	155.40	155.46
	53.43	53.47		—	155.56
7	58.02	58.36	20	163.28	163.74
	61.07	61.11		163.22	163.60
8	64.15	64.33			
	67.18	67.07	21	171.38	171.57
9	88.27	88.37		171.57	171.76
	75.82	75.85	22	179.27	179.26
10	96.84	96.38		179.38	179.57
	83.92	83.90	23	187.02	187.25
				187.34	187.43
11	87.89	87.88	24	195.13	195.12
	91.70	92.08		195.16	195.29
12	97.58	97.69	25	—	203.02
	99.83	100.05		—	203.22
13	106.49	106.56	26	210.93	—
	107.86	108.01		211.02	—

TABLE II.—(*Continued*).

$\Delta_2 T'(K)$ VALUES

$v' = 5$

K	Parker†	(5–7) λ4486	K	Parker†	(5–7) λ4486
1	—	—	13	104.56	104.25
	—	—		—	104.70
2	—	19.10*	14	—	112.05
	—	19.58		—	112.30
3	—	24.12*	15	120.07	119.97
	25.16	26.75		—	120.01
4	—	28.83*			
	34.01	34.23	16	—	127.49
5	42.41	—*		—	127.85
	—	42.05	17	—	135.29
	—	39.27*		—	135.76
			18	—	142.94
6	50.23	49.40*		—	143.27
	—	50.29	19	—	151.00
7	—*	57.66		—	150.65
	—	58.03	20	—	158.38
8	65.73	65.21		—	158.37
	—	65.90			
9	73.73	73.29	21	—	—
	—	73.66		—	—
10	81.36	80.97	22	—	173.27
	—	81.34		—	173.22
			23	—	—
11	89.04	88.82		—	—
	—	89.17	24	—	188.90
12	97.10	96.51		—	189.12
	—	96.79			

† Values from 5–8 band.

* Perturbed lines immediately before and after point of greatest displacement.

TABLE II.—(*Continued*).

$\Delta_2 T'(K)$ VALUES

$v' = 6$

K	Parker*	(6–8) λ4466.6	K	Parker*	(6–8) λ4466.6
1	11.10	11.37	11	—	87.34
2	17.85	19.03	12	94.99	94.93
3	—	26.63	13	102.90	102.35
4	34.28	34.19	14	110.10	110.05
5	42.08	41.91	15	117.57	117.66
6	49.69	49.83	16	125.28	125.46
7	57.27	57.17	17	132.72	132.88
8	64.71	64.63	18	140.01	140.24
9	72.27	72.14	19	—	147.98
10	80.19	79.80	20	—	155.34
			21	—	163.00

TABLE III.

$\Delta_2 T''(K)$ VALUES

$v'' = 2$

K	Average†	(2–2) λ3857.9	K	Average†	(2–2) λ3857.9
1	11.30	11.26	11	86.63	86.45
2	18.74	18.68	12	94.19	94.18
3	26.34	26.55	13	101.64	101.55
4	33.96	33.72	14	109.26	108.93
5	41.54	41.52	15	116.70	116.50
6	49.00	48.91	16	124.15	124.11.
7	56.51	56.59	17	131.59	131.60
8	64.07	64.19	18	139.10	139.25
9	71.58	71.71	19	146.55	146.75
10	79.04	79.16	20	154.02	154.12

* Values from (6–9) band.

† Average from λλ4709.3 and 4236.5.

TABLE III.—(*Continued*).

$\Delta_2 T''(K)$ VALUES

$v'' = 3$

K	(0–3) 5228.3	(1–3) 4651.9	(2–3) 4199.2	K	(0–3) 5228.3	(1–3) 4651.9	(2–3) 4199.2
1	11.21	11.39	11.12	20	152.49	152.53	152.47
2	18.59	18.19	18.49		—	152.50	—
3	26.16	26.60	26.03				
4	33.32	33.61	33.44	21	159.90	160.11	159.65
5	40.97	40.99	40.87		159.79	159.90	—
				22	167.18	167.30	167.27
6	48.32	48.49	48.41		167.32	167.37	—
7	55.82	55.97	55.86	23	174.67	174.73	174.66
8	63.30	63.28	63.33		174.82	175.03	—
9	70.80	70.38	70.74	24	181.99	182.07	—
10	78.35	78.37	78.28		182.18	182.29	—
	—	—	—	25	189.37	189.49	—
11	85.87	85.78	85.58		189.44	189.61	—
	—	85.77	—				
12	93.26	93.22	93.20	26	—	197.71	—
	—	93.26	—		—	197.67	—
13	100.88	100.71	100.52	27	—	204.18	—
	—	100.80	—		—	204.40	—
14	108.14	107.85	108.00	28	—	210.62	—
	—	107.87	—		—	210.51	—
15	115.52	115.53	115.41	29	—	218.81	—
	—	115.46	—		—	219.00	—
				30	—	225.84	—
16	123.03	122.88	122.80		—	226.21	—
	—	122.98	—				
17	130.62	130.33	130.26	31	—	233.38	—
	—	130.05	—		—	233.12	—
18	137.83	137.82	137.68	32	—	240.79	—
	—	137.84	—		—	240.56	—
19	145.17	145.11	145.10	33	—	248.29	—
	—	145.07	—		—	248.11	—

TABLE III.—(*Continued*).

$\Delta_2 T''(K)$ VALUES

$v'' = 4$

K	(1–4) 5148.8	(2–4) 4599.9	(3–4) 4166.8 4166.4
1	11.05	11.01	11.03
2	—	18.46	18.51
	—	—	18.50
3	25.94	25.54	25.90
	—	—	25.83
4	32.99	33.22	33.26
	—	—	33.18
5	40.55	40.64	40.57
	—	—	40.62
6	48.05	48.16	48.02
	—	—	48.14
7	55.30	55.30	55.25
	—	—	55.31
8	62.67	63.04	62.70
	—	—	62.62
9	70.07	69.98	70.08
	—	—	70.02
	—	—	70.20
10	77.48	77.27	77.37
	—	—	77.22
11	85.07	84.97	85.23
	84.88	—	84.76
12	92.25	91.93	92.06
	92.22	—	92.13
13	99.56	99.26	99.46
	99.79	—	99.40
14	106.89	106.76	106.99
	106.81	—	106.77
15	114.09	114.17	114.24
	114.03	—	114.14

K	(1–4) 5148.8	(2–4) 4599.9	(3–4) 4166.8 4166.4
16	121.53	121.48	121.26
	121.61	—	121.54
17	128.91	129.16	128.95
	128.99	—	128.86
18	136.50	136.06	136.22
	136.20	—	136.28
19	—	143.34	143.41
	—	—	143.31
20	—	150.81	151.01
	—	—	—
21	—	158.26	158.20
	—	—	158.19
22	—	165.52	165.42
	—	—	165.55
23	—	172.83	172.86
	—	—	172.75
24	—	180.08	—
	—	—	—
25	—	187.39	187.43
	—	—	187.41
26	—	194.67	—
	—	—	—
27	—	202.09	201.93
	—	—	201.98
28	—	209.20	—
29	—	215.72	—
30	—	223.46	—
31	—	231.34	—
32	—	239.04	—
33	—	246.28	—

TABLE III.—(*Continued*).

$\Delta_2 T''(K)$ VALUES

$v'' = 5$

K	(2–5) 5076.5	(3–5) 4554.4 4553.2	K	(2–5) 5076.5	(3–5) 4554.4 4553.2
1	(10.90)	—	13	98.34	98.48
	—	11.15		—	98.43
2	18.32	18.36	14	105.72	105.77
	—	18.30		—	105.81
3	25.75	25.48	15	112.82	113.13
	—	25.43		—	113.05
4	32.99	32.54			
	—	32.69	16	119.81	120.20
5	40.26	40.28		—	120.23
	—	40.23	17	127.33	127.49
				—	127.49
6	47.55	47.80	18	134.75	134.77
	—	47.66		—	134.66
7	54.69	54.79	19	142.30	142.25
	—	54.72		—	142.02
8	61.91	62.19	20	(149.42)	149.32
	—	62.10		—	149.33
9	69.27	69.53			
	—	69.27	21	156.46	156.59
10	76.48	76.53		—	156.58
	—	76.44	22	163.98	164.02
				—	163.99
11	83.10	83.94	23	—	170.97
	—	83.90		—	171.05
12	90.95	91.08	24	—	178.23
	—	91.49		—	178.33

( ) Calculated from interpolated R lines.

TABLE III.—(*Continued*).

$\Delta_2 T''(K)$ VALUES

$v'' = 7$

K	Parker†	(5–7) λ4486	K	Parker†	(5–7) λ4486
1	10.79	—	13	96.14	96.23
2	17.97	—		—	96.18
3	25.08	24.70	14	103.39	103.59
	—	24.83		—	103.42
4	32.48	31.92	15	110.66	110.54
	—	32.00		—	110.72
	—	31.99			
5	39.43	39.29	16	117.68	117.65
	—	39.01		—	118.06
			17	124.75	124.65
6	46.43	46.29		—	124.87
	—	46.12	18	131.57	131.83
7	53.62	53.31		—	131.69
	—	53.58	19	138.90	138.94
8	—	60.79		—	138.77
	—	60.73	20	146.09	—
9	67.83	67.74		—	—
	—	67.76			
10	—	74.99	21	153.02	152.59
	—	74.94		—	152.77
			22	—	—
11	82.00	82.01		—	—
	—	81.95	23	—	166.93
12	89.11	89.10		—	167.11
	—	89.17			

$v'' = 8$

K	Average*	(6–8) λ4466.6	K	Average*	(6–8) λ4466.6
1	10.80	10.61	6	45.99	45.93
2	17.89	17.68	7	52.88	52.93
3	24.57	24.64	8	60.19	59.97
4	30.89	31.85	9	67.01	67.05
5	38.81	39.21	10	74.13	74.00

† From (4–7) band.

* Average of results of Coster and Brons (10–8) and Parker (5–8).

TABLE III.—(*Continued*).

$\Delta_2 T''(K)$ VALUES

$v'' = 8$—(*Continued*).

K	Average*	(6–8) λ4466.6	K	Average*	(6–8) λ4466.6
11	81.34	80.93	16	116.29	116.27
12	88.35	88.01	17	—	123.05
13	95.14	95.19	18	—	130.46
14	102.22	102.35	19	—	137.51
15	109.27	109.79	20	—	144.11

TABLE IV.

THEORETICAL AND OBSERVED ORIGINS.

Band	Observed	Calculated†
(2–2)	25939.8	25939.8
(3–4)	24013.9	24014.5
(3–5)	21971.1	21971.6
(5–7)	22305.4	22305.0
(6–8)	22406.5	22404.0
(0–3)	19139.7	19139.8
(1–4)	19434.7	19434.6
(2–5)	19710.4	19711.6

* Average of results of Coster and Brons (10–8) and Parker (5–8).

† These are calculated from the expression $\nu = 25566.0 + 2396.22v' - 24.070v'^2 - 0.6365v'^3 - .04949v'^4 - (2191.02v'' - 16.196v''^2 - 0.0400v''^3)$ given by Coster and Brons.

TABLE V.

VALUES OF B_v' AND B_v''

v	B_v' (Parker)*	B_v'' (C & B)*	B_v' (C & T)	B_v'' (C & T)
0	2.074		2.073	
1	2.052		2.051	
2	2.028	1.880	2.026	1.879
3	1.998	1.860	2.004	1.863
4		1.840		1.843
5	1.932	1.820	1.926	1.826
6	1.895		1.897	
7		1.780		1.780
8		1.760		1.768

* Values of B_v' and B_v'' as calculated from expressions given by Parker and Coster and Brons respectively compared with values measured by us.

TABLE VI.

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII
	Smoothed Values	Observed $R_1(K)$	$R_2(K)$	K'		Smoothed Values	Observed $P_1(K)$	$P_2(K)$	(III–II)	(VIII –VII)	(IV–II)	(IX–VII)
						Origin 21970.81						
Origin	21970.81	—		0	P(1)	67.10	21966.60	—	− .50			
R(0)	74.88	21974.49	—	1	P(2)	63.77	63.34	63.77	− .39	− .43	0.0	0.0
R(1)	79.26	78.74	21979.26	2	P(3)	60.90	60.44	60.90	− .52	− .46	0.0	0.0
R(2)	83.97	83.14	83.82	3	P(4)	58.42	57.66	58.39	− .83	− .76	− .15	− .03
R(3)	89.11	88.17	89.11	4	P(5)	56.39	55.26	56.42	− .94	−1.13	0	+ .04
R(4)	21994.60	93.30	94.50	5	P(6)	54.53	53.02	54.27	−1.30	−1.51	− .10	− .26
R(5)	22000.54	98.62	22000.06	6	P(7)	53.06	50.82	52.40	−1.92	−2.24	− .48	− .66
R(6)	06.74	22003.97	07.74	7	P(8)	52.05	49.18	53.02	−2.77	−2.87	+1.00	+ .97
R(7)	13.33	09.18	13.51	8	P(9)	51.30	46.99	51.41	−4.15	−4.31	+ .18	+ .11
R(8)	20.09	13.51	20.09	9	P(10)	50.85	43.98	50.82	−6.58	−6.87	0.0	− .03
R(9)	27.26	35.36		10	P(11)	50.82	58.83	50.82	+8.10	+8.01	0.0	0.0
R(10)	34.72	40.36		11	P(12)	50.82	56.42		+5.64	+5.60		
R(11)	42.90	46.71		12	P(13)	51.41	55.63		+3.81	+4.22		
R(12)	50.87	54.11		13	P(14)	52.40	55.63		+3.24	+3.23		
R(13)	59.42	62.19		14	P(15)	53.61	56.42		+2.77	+2.81		
R(14)	68.31	70.79		15	P(16)	55.26	57.66		+2.48	+2.40		
R(15)	77.50	79.55		16	P(17)	57.27	59.35		+2.05	+2.08		
R(16)	87.06	88.96		17	P(18)	59.57	61.47		+1.90	+1.90		
R(17)	96.94	98.73		18	P(19)	62.28	63.96		+1.79	+1.78		
R(18)	22107.25	22108.85		19	P(20)	65.23	66.60†		+1.60	+1.37		
R(19)	17.84	19.42		20	P(21)	68.51	70.10		+1.58	1.59		

† Superposed by another line.

TABLE VII.

	I	II	III	IV	V
	Smoothed $\Delta_2 T(K)$ values	($\Delta_2 T_1$ obs. $-\Delta_2 T_{smoothed}$) (3–5)	(3–4)	($\Delta_2 T_2$ obs. $-\Delta_2 T_{smoothed}$) (3–5)	(3–4)
1	12.03	+0.11	+0.23	—	—
2	20.04	−0.24	−0.11	+0.01	−0.02
3	28.06	−0.33	−0.25	+0.15	+0.12
4	36.06	−0.42	−0.48	+0.02	−0.05
5	44.04	−0.68	−0.72	−0.40	−0.27
6	52.02	−1.07	−1.21	+1.45	+1.41
7	60.00	−1.64	−1.98	+1.11	+1.07
8	67.97	−3.64	−3.84	−0.92	−0.79
9	75.94	+12.43	+12.33	−0.11	−0.12
10	83.91	+12.47	+12.43	+0.01	−0.01
11	91.88	−4.00	−3.99	0.0	0.0
12	99.94	−2.25	−2.36		
13	107.93	−1.37	−1.44		
14	115.87	−0.71	−0.87		
15	123.86	−0.73	−0.72		
16	131.76	−0.46	−0.42		
17	139.70	−0.32	−0.39		
18	147.69	−0.31	−0.29		
19	155.56	−0.10	−0.16		